

AD-A182 617

PREPARATION AND CHARACTERIZATION OF THE QUATERNARY
CHALCOGENIDES $Cu_2O(II)$. (U) BROWN UNIV PROVIDENCE RI
DEPT OF CHEMISTRY G Q YAO ET AL. 06 JUL 87 TR-3

1/1

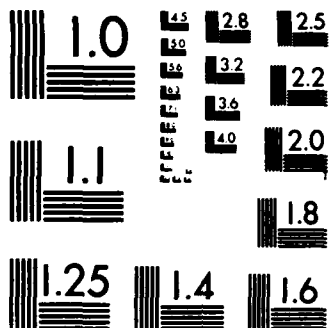
UNCLASSIFIED

NO0014-85-K-8177

F/G 7/2

NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

AD-A182 617

(12)

DTIC FILE COPY

OFFICE OF NAVAL RESEARCH

Contract N00014-85-0177

R & T Code 431a003

Technical Report No. 3

Preparation and Characterization of the Quaternary Chalcogenides

$\text{Cu}_2\text{B(II)C(IV)X}_4$ [B(II) = Zn, Cd; C(IV) = Si, Ge; X = S, Se]

by

G.Q. Yao, H-S. Shen, E. D. Honig, R. Kershaw, K. Dwight, A. Wold

Prepared for Publication in

Solid State Ionics

DTIC
ELECTE
JUL 15 1987
S D

Brown University
Department of Chemistry
Providence, RI 02912

July 6, 1987

Reproduction in whole or in part is permitted for any purpose of the
United States Government.

This document has been approved for public release and sale;
its distribution is unlimited

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release: distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4. PERFORMING ORGANIZATION REPORT NUMBER(S) #3		5. MONITORING ORGANIZATION REPORT NUMBER(S) NO0014-85-K-0177	
6a. NAME OF PERFORMING ORGANIZATION Aaron wold Brown University	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research Dr. R. Schwartz	
6c. ADDRESS (City, State, and ZIP Code) Chemistry Department, Box D Providence RI 02912		7b. ADDRESS (City, State, and ZIP Code) Code 3854 NWC China Lake, CA 93555	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO TASK NO NR 700 003
11. TITLE (Include Security Classification) PREPARATION AND CHARACTERIZATION OF THE QUATERNARY CHALCOGENIDES $Cu_2B(II)C(IV)X_4$ [B(II) = ZnCd; C(IV) = Si, Ge; X = S, Se]			
12. PERSONAL AUTHOR(S) G.Q. Yao, H-S. Shen, E.D. Honig, R. Kershaw, K. Dwight, A. Wold			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM TO	14. DATE OF REPORT (Year, Month, Day) July 7, 1987	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION SUBMITTED FOR PUBLICATION IN SOLID STATE IONICS			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) A number of quaternary chalcogenides crystallizing with the wurtz-stannite structure have been prepared by chemical vapor transport and characterized. Cu_2ZnGeS_4 and $Cu_2ZnSiSe_4$ transmit in the infrared beyond 12 microns. Cu_2ZnGeS_4 was stable in air up to 620°C and also was the hardest of all the materials studied <i>(Key words: Copper Chalcogenides, Zinc, Silicon)</i>			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input type="checkbox"/> UNCLASSIFIED UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION	
22a. NAME OF RESPONSIBLE INDIVIDUAL		22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

PREPARATION AND CHARACTERIZATION OF THE QUATERNARY CHALCOGENIDES
 $\text{Cu}_2\text{B(II)C(IV)X}_4$ [B(II) = Zn,Cd; C(IV) = Si,Ge; X = S,Se]

G-Q. Yao, H-S. Shen, E. D. Honig, R. Kershaw, K. Dwight, A. Wold*
Chemistry Department, Brown University
Providence, Rhode Island 02912

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



A number of quaternary chalcogenides crystallizing with the wurtz-stannite structure have been prepared by chemical vapor transport and characterized. $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{ZnSiSe}_4$ transmit in the infrared beyond 12 microns. $\text{Cu}_2\text{ZnGeS}_4$ was stable in air up to 620°C and also was the hardest of all the materials studied.

1. INTRODUCTION

In recent years, compounds crystallizing with the chalcopyrite structure have been studied in order to observe their optical and semiconducting properties. However, only a relatively few studies have been reported concerning the characterization of quaternary chalcogenides crystallizing with the stannite structure. The compounds $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$, $\text{Cu}_2\text{ZnGeS}_4$ and $\text{Cu}_2\text{CdSiS}_4$ are semiconductors which crystallize with the orthorhombic superstructure of wurtzite called the wurtz-stannite structure (1-4) space group $\text{Pmn}2_1$, shown in Fig. 1. In this structure there are alternating cation layers of mixed B(II) and C(IV) atoms, which are separated by layers of Cu atoms. The structure is therefore derived from an ordering of the cations of the wurtzite cell. In this structure, every sulfur or selenium has four nearest neighbor metal atoms at the corners of the surrounding tetrahedron, two copper atoms, one zinc or cadmium atom, and either a silicon or germanium atom.

Single crystals of these compounds have been grown by chemical vapor transport using iodine as the transport agent (1-4). Several publications report their magnetic, electrical and optical properties (4-6). However, there has been no report concerning their hardness, thermal stability or their transmission in the infrared. It was of interest to measure these properties and correlate them with the substitutions made for the Group II, Group IV and Group VI elements.

2. EXPERIMENTAL

Single crystal growth.

Single crystals of the quaternary chalcogenides were all prepared by chemical vapor transport using iodine as the transport agent. The stoichiometric weights of the elements were introduced into silica tubes which were evacuated to 5×10^{-5} torr. Five mg/cc of iodine were added to the transport tube which was then sealed and the tube set in the back transport mode and run in this mode for two days. Optimum crystal growth of $\text{Cu}_2\text{ZnGeS}_4$,

$\text{Cu}_2\text{CdSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$ occurred when the charge zone was maintained at 850°C and the growth zone at 800°C . The transport temperature was 950°C at the charge zone and 900°C at the growth zone for crystal growth of $\text{Cu}_2\text{ZnSiS}_4$. The transport process was carried out for two weeks. Polyhedral crystals $2 \times 2 \times 3 \text{ mm}^3$ of $\text{Cu}_2\text{ZnGeS}_4$ and blade crystals $2 \times 1 \times 7 \text{ mm}^3$ of $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$ and $\text{Cu}_2\text{CdSiS}_4$ were obtained.

Powder diffraction patterns of ground single crystals were obtained with a Norelco diffractometer using monochromatic radiation from a high-intensity copper source ($\lambda\text{-CuK}\alpha_1 = 1.5405\text{\AA}$). Cell parameters were determined from slow-scan ($0.25^\circ/\text{min}$) diffraction patterns over the range $12^\circ < 2\theta < 72^\circ$. The precise cell parameters were obtained using a least-squares refinement from these reflections.

Optical and electrical measurements.

Infrared transmission measurements were made on polished single-crystal slices at room temperature using a Perkins-Elmer 580 single beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range $2.5\mu\text{m} - 25\mu\text{m}$. Transmission through the sample was normalized to the signal obtained in the absence of the sample.

Measurements of absorption coefficients were made with an Oriel Model 1724 monochromator, an Oriel G 772-5400 long pass filter, and a calibrated silicon diode detector. Absorption values were calculated from the responses with and without the crystal in the beam.

The van der Pauw (7) method was used to measure electrical resistivities from 77K to 400K. Contacts were made by the ultrasonic soldering of indium onto the samples, and ohmic behavior was established by measuring the current-voltage characteristics.

3. RESULTS AND DISCUSSION

Single crystals of $\text{Cu}_2\text{ZnSiS}_4$, $\text{Cu}_2\text{ZnSiSe}_4$, $\text{Cu}_2\text{ZnGeS}_4$, $\text{Cu}_2\text{CdSiS}_4$, $\text{Cu}_2\text{ZnGeSe}_4$ and $\text{Cu}_2\text{CdGeSe}_4$ have been grown by chemical vapor transport using iodine as the transport agent. The first

four compounds showed transmission in the infrared region and were therefore studied in detail. A relatively high transport temperature (950°C - 900°C) was used to grow $\text{Cu}_2\text{ZnSiS}_4$ single crystals because at lower temperatures (850°C - 800°C) the major phase obtained at the growth zone was ZnS.

X-ray diffraction analysis confirmed the cell parameters (Table 1) of these quaternary chalcogenides previously reported (3, 4, 6).

The microhardness measurements (Knoop indenter) were made on crystals using a Kentron Microhardness Tester. The results were obtained using a diamond indenter with a 100 g load and are given in Table 1.

The stability of these compounds toward oxidation was determined by heating them in a flowing oxygen stream (65 cc/min) and determining the change in weight during the heating period. The results shown in Table 1 indicate that $\text{Cu}_2\text{ZnSiS}_4$ decomposes at a higher temperature than the selenide $\text{Cu}_2\text{ZnSiSe}_4$. Furthermore $\text{Cu}_2\text{ZnSiS}_4$ is more stable than $\text{Cu}_2\text{CdSiS}_4$. A comparison of the relative thermal stability of $\text{Cu}_2\text{ZnSiS}_4$ and $\text{Cu}_2\text{ZnGeS}_4$ is shown in Fig. 2. It can be seen that the rate of oxidation proceeds much slower for the former compound. These results are consistent with the anticipated increased stability of sulfides vs selenides and silicon vs germanium or zinc vs cadmium chalcogenides.

A comparison of the infrared absorption bands can also be made by examining the results summarized in Table 1 and Figs. 3 and 4. It can be seen that the substitution of selenium for sulfur shifts the absorption bands to higher wavelengths. The substitution of germanium for silicon also results in a shift of the bands to higher wavelengths but in addition the absorption peaks occur much closer together.

The indirect optical band gaps were obtained from plots of $(\alpha h\nu)^{1/2}$ vs energy and are given in Table 1. $\text{Cu}_2\text{ZnSiS}_4$ was observed to show the largest band gap (3.04 eV) and there was a marked decrease in the band gap when either a larger cation (Cd or Ge) or anion (Se) was substituted for Zn, Si or S. The resistivities

for the four chalcogenides are also given in Table 1 and the lower resistivity of the cadmium compound is consistent with the electronic properties of other cadmium chalcogenides.

4. ACKNOWLEDGMENTS

This research has been partially supported by the Office of Naval Research. The authors also wish to acknowledge the National Science Foundation Grant No. NSF Grant No. DMR-820-3667 for the partial support of K. Dwight and they express their appreciation for the use of Brown University's Materials Research Laboratory which is supported by the National Science Foundation.

7

*Address all correspondence

5. REFERENCES

1. H. Hahn and H. Schulze, Naturwissenschaften 52, 426 (1965).
2. R. Nitsche, D. F. Sargent and P. Wild, J. Cryst. Growth 1, 52 (1967).
3. W. Schafer and R. N. Nitsche, Mat. Res. Bull., 9, 645 (1974).
4. D. M. Schleich and A. Wold, Mat. Res. Bull., 12, 111 (1977).
5. L. Guen, W. S. Glaunsinger and A. Wold, Mat. Res. Bull., 14, 463 (1979).
6. L. Guen and W. S. Glaunsinger, J. Solid State Chem., 35, 10 (1980).
7. J. van der Pauw, Philips Res. Rep., 13, 11 (1958).

FIGURE CAPTIONS

Fig. 1.

The wurtz-stannite structure.

Fig. 2.

Comparison of the stability toward oxidation in O_2 of ground crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 .

Fig. 3.

Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and $Cu_2ZnSiSe_4$, normalized to a thickness of 0.11 mm assuming no reflection or scattering.

Fig. 4.

Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 , normalized to a thickness of 0.11 mm assuming no reflection or scattering.

FIGURE CAPTIONS

Fig. 1.
The wurtz-stannite structure.

Fig. 2.
Comparison of the stability toward oxidation in O_2 of ground crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 .

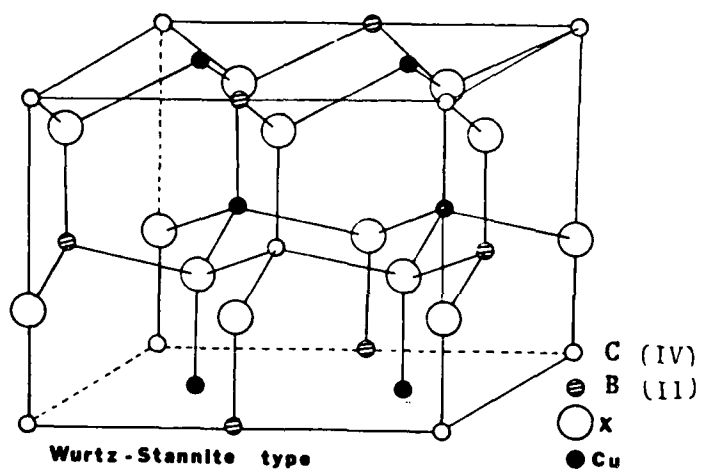
Fig. 3.
Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and $Cu_2ZnSiSe_4$, normalized to a thickness of 0.11 mm assuming no reflection or scattering.

Fig. 4.
Comparison of the infrared transmission spectra of polished crystals of Cu_2ZnSiS_4 and Cu_2ZnGeS_4 , normalized to a thickness of 0.11 mm assuming no reflection or scattering.

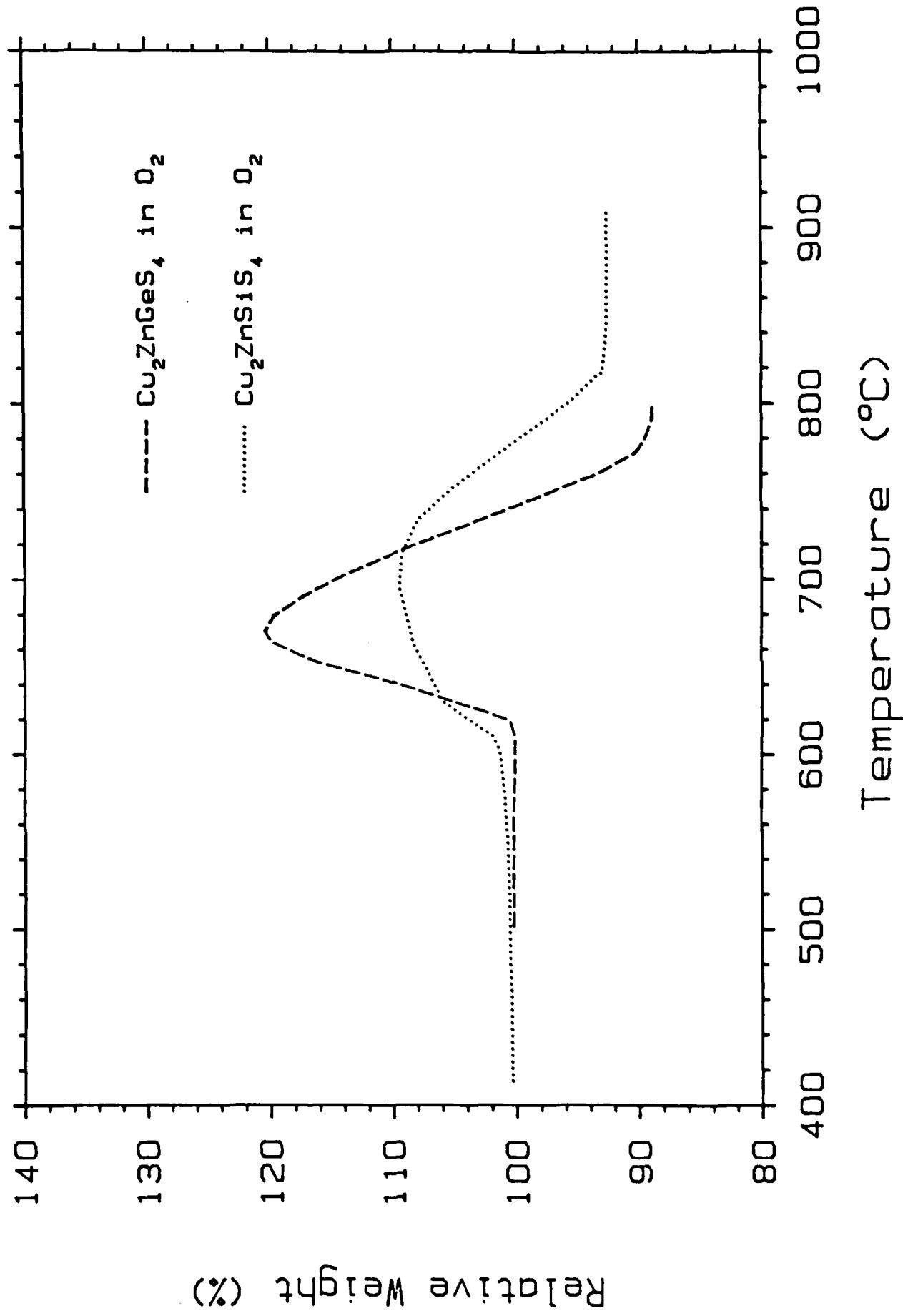
TABLE 1. PROPERTIES OF SOME QUATERNARY CHALCOGENIDES

Compound	Cell Parameter		(R-T) (Ω -cm)	E _g (e.v.)	IR Absorption bands (μ)	Knoop* Hardness kg/mm ²	Decomposition Temperature C° \pm 10)
Cu ₂ ZnSiS ₄ (orth)	A	B	C				
	7.436(1)	6.398(1)	6.137(2)	Insulator	3.04(2)	7.9(w) 9.7, 11.1	620
Cu ₂ ZnGeS ₄ (orth)	A	B	C				
	7.506(3)	6.476(4)	6.189(2)	1.6 x 10 ⁴	2.04(2)	12.6, 13.2	620
Cu ₂ ZnSiSe ₄ (orth)	A	B	C				
	7.826(3)	6.727(2)	6.445(1)	3 x 10 ⁴	2.20(2)	12, 15.3	470
Cu ₂ CdSiS ₄ (orth)	A	B	C				
	7.609(1)	6.485(1)	6.251(1)	48	2.0 2.45(5)	9.7, 11.1 12.5(w)	510

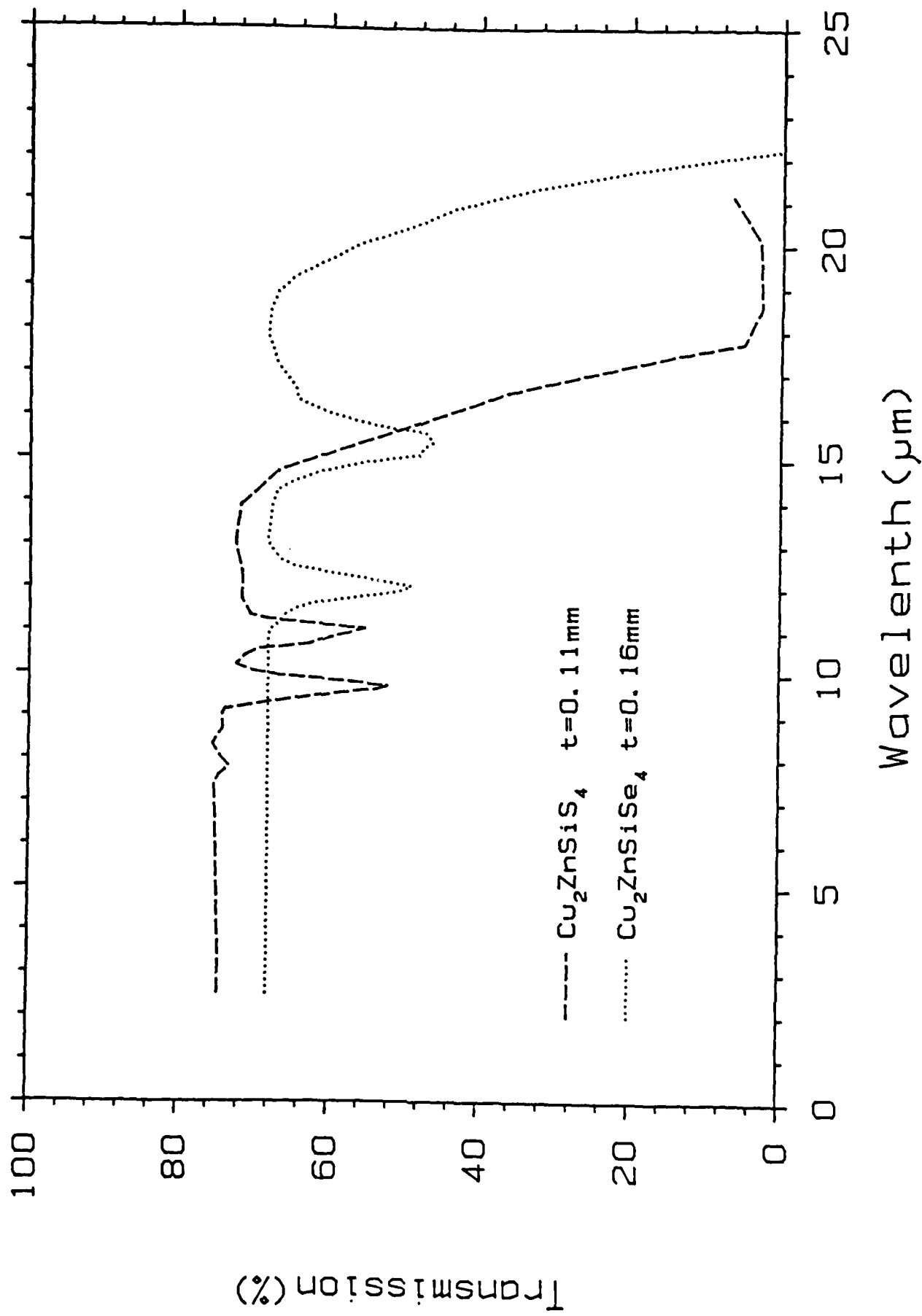
*Knoop indenter at 100g, lowered slowly. Hardness values \pm 100.



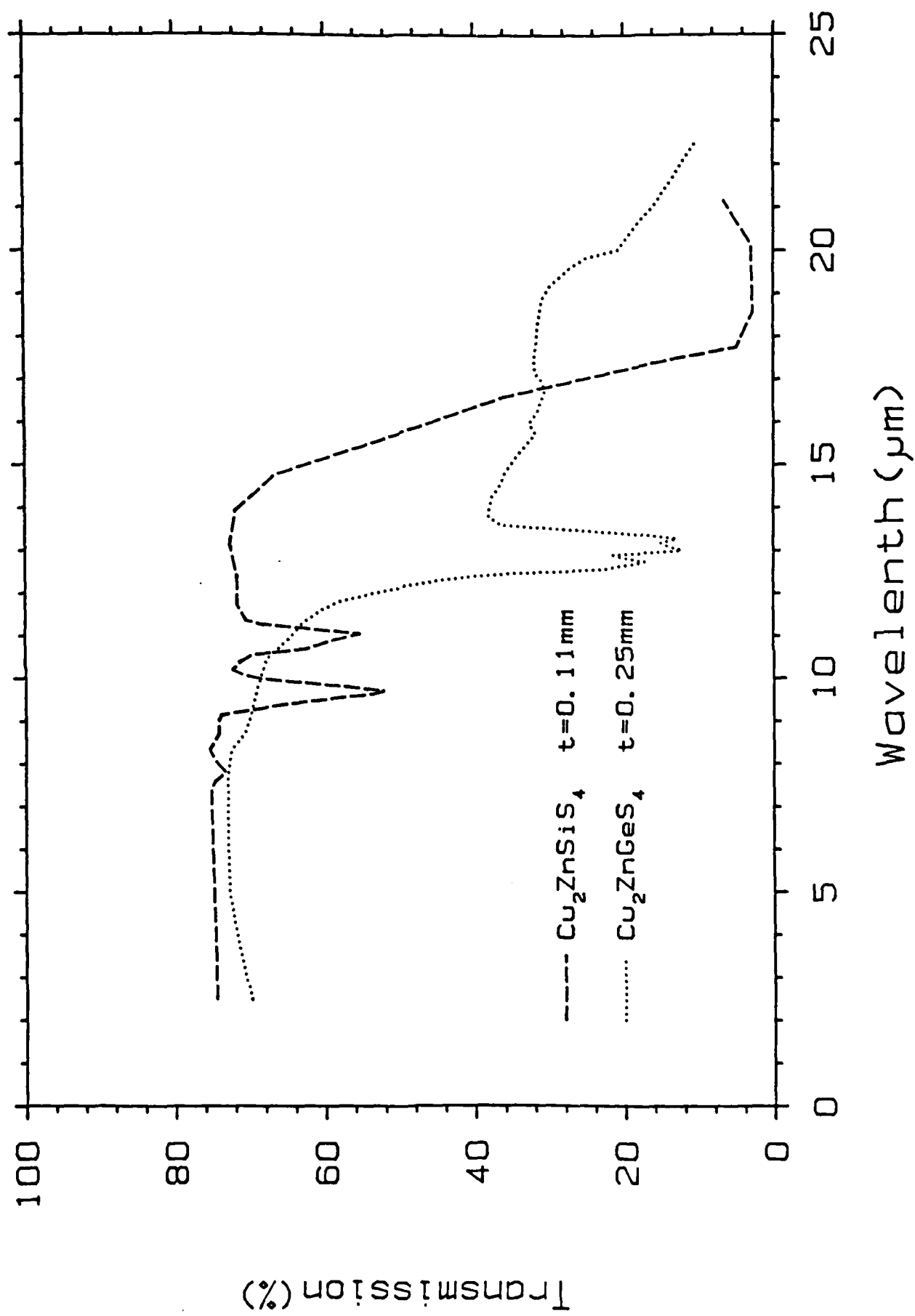
THERMOGRAVIMETRIC ANALYSIS



IR SPECTRUM



IR SPECTRUM



Office of Naval Research
Attn: Code 1113
800 N. Quincy Street
Arlington, VA 22217-5000

Naval Ocean Systems Center
Attn: Dr. S. Yamamoto
Marine Sciences Division
San Diego, CA 91232

SP-11-2
July 67
General
21

Dr. Bernard Douda
Naval Weapons Support Center
Code 50C
Crane, Indiana 47511-5050

Naval Civil Engineering Lab
Attn: Dr. R. W. Drisko
Code L52
Port Hueneme, CA 93401

Defense Technical Information
Center, Building 5
Cameron Station
Alexandria, VA 22314

DTNSRDC
Attn: Dr. H. Singerman
Applied Chemistry Division
Annapolis, MD 21401

Dr. William Tolles
Superintendent
Chemistry Division, Code 6100
Naval Research Lab
Washington D.C. 20375-5000

Dr. David Young
Code 334
NORDA
NSTL, Mississippi 39529

Naval Weapons Center
Attn: Dr. Ron Atkins
Chemistry Division
China Lake, CA 93555

Scientific Advisor
Commandant of the Marine Corps
Code RD-1
Washington, D.C. 20380

U.S. Army Research Office
Attn: CRD-AA-IP
P. O. Box 12211
Research Triangle park, NC 27709

Mr. John Boyle
Materials Branch
Naval Ship Engineering Ctr.
Philadelphia, PA 19112

Dr. Karl Prese, Jr.
SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025

Dr. N. John Cooper
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260

Dr. Aaron Fletcher
Code 3852
Naval Weapons Center
China Lake, CA 93555

Dr. S. D. Worley
Department of Chemistry
Auburn University
Auburn, Alabama 36830

Dr. J. Cooper
Code 6170
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Thomas J. Meyer
Department of Chemistry
University of North Carolina
Chapel Hill, NC 27514

Dr. M. C. Baird
Department of Chemistry
Queens's University
Kingston, Canada
K7L 3N6

Dr. Jeffrey Zink
Department of Chemistry
University of California
Los Angeles, CA 90024

Dr. N. N. Lichtin
Department of Chemistry
Boston University
685 Commonwealth Ave
Boston, MA 02215

Dr. R. Eisenberg
Dept. of Chemistry
University of Rochester
Rochester, NY 14627

Dr. Alan R. Cutler
Department of Chemistry
RPI
Troy, NY 12180-3590

Dr. L. Vaska
Department of Chemistry
Clarkson College
Potsdam, NY 13676

Dr. R. A. Huggins
Materials Science and Engineer-
ing Dept.
Stanford University
Stanford, CA 94305

Dr. Carlo Floriani
Minerale et Analytique
Universite de Lausanne
Place du Chateau 3
Lausanne, Switzerland

Dr. Wiley Youngs
Department of Chemistry
Case Western Reserve U.
Cleveland, OH 44106

15 K-2
687

END

8-87

DTIC